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(54) LITHIUM MANGANATE PARTICLE POWDER AND ITS MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium manganate particle powder used as a positive-electrode active material for a nonaqueous electrolyte secondary battery and giving excellent charging/discharging characteristics to the secondary battery.

SOLUTION: This lithium manganate particle powder comprises primary particles of 0.05 to 5.0 μm in average particle diameter and contains LiMn2O4 and Li2MnO3. With respect to peak strength in X-ray diffraction of the powder, the peak strength of a (133) plane of the Li2MnO3 is more than 0 but not more than 0.05 relative to the peak strength of a (400) plane of the LiMn2O4. The powder is obtained by mixing manganese oxide and a lithium compound, primarily baking the mixture at temperatures in the range of 850 to 1,000°C, and then secondarily baking it at temperatures in the range of 700 to 800°C.

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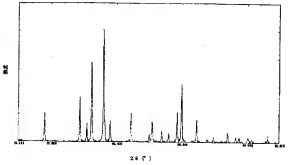
CLAIMS

[Claim(s)]
[Claim 1] Manganic acid lithium particle powder which is manganic acid lithium particle powder containing LiMn 2O4 which consists of a primary particle with a mean particle diameter of 0.05-5.0 micrometers, and Li2MnO3, and the peak intensity of said field (133) of Li2MnO3 exceeds 0 to the peak intensity of the field (400) of said LiMn 2O4, and is characterized by being 0.05 or less in the peak intensity of the X diffraction of this manganic acid lithium particle powder.
[Claim 2] The manufacturing method of the manganic acid lithium particle powder according to claim 1 characterized by calcinating secondarily in a 700-800-degree C temperature requirement after mixing a manganic acid ghost and a lithium compound and calcinating this mixture primarily in a 850-1000-degree C temperature requirement.

[Translation done.]

Drawing selection drawing 1



[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the manganic acid lithium particle powder which was excellent in the charge-and-discharge cycle property of a rechargeable battery as positive active material for nonaqueous electrolyte rechargeable batteries.
[0002]
[Description of the Prior Art] In recent years, portable-izing of electronic equipment, such as an AV equipment and a personal computer, and cordless-ization are progressing quickly, and small and the demand to the rechargeable battery which is lightweight and has a high energy consistency are high as these power sources for a drive. Charge and discharge voltage is high under such a situation, and the rechargeable lithium-ion battery which has the advantage in which charge-and-discharge capacity is also large attracts attention.
[0003] Conventionally, as positive active material useful to the rechargeable lithium-ion battery of a high energy mold with a 4V class electrical potential difference, generally LiMn 2O4 of spinel type structure, LiMnO2 and LiCoO2 of rock salt type structure, LiCo1-XNiXO2, and LiNiO2 grade are known, and especially, although LiCoO2 is excellent in the point of having a high voltage and high capacity, it includes the problem of the manufacturing-cost quantity by there being little amount of supply of a cobalt raw material, and the problem on the environmental insurance of an abandonment cell. Then, research of the manganic acid lithium particle powder (basic presentation: LiMn 2O4) of the Spinel structure mold with which many amount of supply is made from low cost considering the good manganese of environmental fitness as a raw material is done briskly.
[0004] As everyone knows, manganic acid lithium particle powder can mix a manganese compound and a lithium compound at a predetermined rate, and can obtain them by calcinating in a 700-800-degree C temperature requirement.
[0005] However, although it has a high voltage and a high energy consistency when manganic acid lithium particle powder is used as positive active material of a rechargeable lithium-ion battery, there is a problem that a charge-and-discharge cycle property is inferior. It is supposed that Mn dissolves this cause into that a crystal lattice expands and contracts by desorption / insertion behavior of the lithium ion in the crystal structure accompanying the repeat of charge and discharge, and grid destruction arises by the volume change of a crystal or the electrolytic solution.
[0006] If it is in the rechargeable lithium-ion battery using manganic acid lithium particle powder, degradation of the charge-and-discharge capacity by the repeat of charge and discharge is controlled, and it is required most now that a charge-and-discharge cycle property should be raised.
[0007] It is required to control the elution of Mn to the inside of to raise the Li/Mn ratio of manganic acid lithium particle powder from one half and the electrolytic solution, in order to raise a charge-and-discharge cycle property, and it is the means. The approach of controlling ** and burning temperature and obtaining the manganic acid lithium particle powder of a high crystal, the approach of adding a different-species element and strengthening the bonding strength of a crystal, the approach of performing surface preparation and controlling the elution of Mn, the approach of controlling the particle size distribution of a manganic acid lithium particle, etc. are performed.
[0008] As an approach of controlling burning temperature to two steps and obtaining manganic acid lithium particle powder, JP,10-241686,A, JP,10-241687,A, and an all directions method given in JP,10-194745,A are learned.
[0009]
[Problem(s) to be Solved by the Invention] The manganic acid lithium particle powder which was excellent in the

charge-and-discharge cycle property of a rechargeable battery as positive active material for nonaqueous electrolyte rechargeable batteries is not yet obtained.

[0010] namely, the above -- after performing primary baking to JP,10-241686,A and JP,10-241687,A above 700 degrees C for the purpose of obtaining the manganic acid lithium particle powder which does not contain an impurity, the method of performing secondary baking at less than 700 degrees C is indicated as it is, but since secondary burning temperature is low temperature as shown in the example of a back appearance comparison, it is hard to call it the manganic acid lithium particle powder excellent in the charge-and-discharge cycle property.

[0011] moreover, the above -- after calcinating primarily to JP,10-194745,A in a 250-900-degree C temperature requirement, the approach of pulverizing with a ball mill and subsequently calcinating secondarily in a 650-800-degree C temperature requirement is indicated by it, but in order to perform intermediate processing intermediate treatment to which crystallinity is reduced after primary baking, the high manganic acid lithium particle powder of crystallinity is difficult to get after secondary baking.

[0012] Then, this invention can control the elution of Mn into the electrolytic solution, and makes it a technical technical problem to offer the manganic acid lithium particle powder which was excellent in the charge-and-discharge cycle property of a rechargeable battery as positive active material for nonaqueous electrolyte rechargeable batteries while it has high crystallinity.

[0013]

[Means for Solving the Problem] This invention as follows can attain said technical technical problem.

[0014] That is, this invention is the manganic acid lithium particle powder containing LiMn 2O4 which consists of a primary particle with a mean particle diameter of 0.05-5.0 micrometers, and Li2MnO3, and is manganic acid lithium particle powder which the peak intensity of said field (133) of Li2MnO3 exceeds 0 to the peak intensity of the field (400) of said LiMn 2O4, and is characterized by being 0.05 or less in the peak intensity of the X diffraction of this manganic acid lithium particle powder.

[0015] Moreover, after this invention mixes a manganic acid ghost and a lithium compound and calcinates this mixture primarily in a 850-1000-degree C temperature requirement, it is the manufacturing method of said manganic acid lithium particle powder characterized by calcinating secondarily in a 700-800-degree C temperature requirement.

[0016] Next, it will be as follows if the configuration of this invention is explained in more detail.

[0017] The mean particle diameter of the primary particle of the manganic acid lithium particle powder concerning this invention is 0.05-5.0 micrometers. When mean particle diameter is less than 0.05 micrometers, the fall of the energy density of a rechargeable battery -- there is the need of pack density becoming low in case the positive electrode of a rechargeable battery is manufactured, and making the amount of binders increasing -- is caused. On the other hand, when exceeding 5.0 micrometers, and current density is made to increase, there is an inclination for the ejection-and-insertion reaction of Li to fall.

[0018] The manganic acid lithium particle powder concerning this invention is expressed with the empirical formula of Li1+xMn2-xO4, and it is desirable that Li/Mn is 0.525-0.6. It is difficult to obtain the manganic acid lithium particle powder of a high crystal [a Li/Mn ratio] when [said] out of range.

[0019] The manganic acid lithium particle powder concerning this invention contains LiMn 2O4 and Li2MnO3, and the ratio of the diffraction reinforcement of the field (133) of Li2MnO3 of the content rate of Li2MnO3 is 0.05 or less exceeding 0 to the diffraction reinforcement of the field (400) of LiMn 2O4 in the diffraction peak intensity of the X diffraction of manganic acid lithium particle powder. When it does not contain Li2MnO3, the reaction of manganic acid lithium particle powder and the electrolytic solution cannot be controlled. When the ratio of diffraction reinforcement exceeds 0.05, since charge-and-discharge capacity falls, it is not desirable. It is 0.01-0.04 preferably.

[0020] In addition, the unusual appearance of Mn 2O3 which does not contribute to charge-and-discharge capacity and a cycle property, Mn3O4, and MnO2 grade may be included.

[0021] The BET specific surface area value of the manganic acid lithium particle powder concerning this invention has desirable 0.1-10m2/g. It is thought that it exfoliates from a plate by telescopic motion of the particle by charge and discharge, and a cell property falls to the case of under 0.1m2/g. In exceeding 10m2/g, reactivity with that the pack density of positive active material falls or the electrolytic solution becomes superfluous, and safety falls.

[0022] The microcrystal size of the manganic acid lithium particle powder concerning this invention has desirable 600A or more. When microcrystal size is less than 600A, it becomes difficult to obtain crystalline high manganic acid lithium particle powder. It is 700A or more preferably.

[0023] The lattice constant of an a-axis has desirable 8.20-8.24A. When the lattice constant of an a-axis is outside

the above-mentioned range, it becomes difficult to obtain crystalline high manganic acid lithium particle powder.

[0024] Next, the manufacturing method of the manganic acid lithium particle powder concerning this invention is described.

[0025] It can cool to 700-800 degrees C as it is, and, subsequently the manganic acid lithium particle powder concerning this invention can be obtained by performing secondary baking at the temperature, after predetermined coming out comparatively, carrying out uniform mixing of a manganese raw material and the lithium raw material and calcinating primarily at 850-1000 degrees C.

[0026] The manganic acid ghost which has structure similar to spinel type structure in an ion array especially is [that what is necessary is just the manganic acid ghost whose mean particle diameter is 0.05-5.0 micrometers as a manganese raw material in this invention] desirable. Specifically, gamma-Mn 2O3 or Mn 3O4 is desirable. Since especially gamma-Mn 2O3 that manufactured the manganese sulfate by the wet composition neutralized and obtained has good reactivity by the particle, it is desirable.

[0027] A lithium carbonate is desirable although a lithium hydroxide, a lithium nitrate, a lithium chloride, etc. can be used as a lithium raw material.

[0028] As for the mixed rate of a manganese raw material and a lithium raw material, considering as about Li/Mn=0.525-0.6 is desirable. Although the capacity of the case of 0.525 or less is high, a charge-and-discharge cycle property falls for generating of distortion by the Jahn-Teller effectiveness. Moreover, the case of 0.6 or more does not have an enough initial capacity.

[0029] It is necessary to make a manganese raw material and a lithium raw material into the uniform mixed state. If homogeneity is not mixed, the manganic acid lithium with which gap of a presentation ratio arises partially and capacity differs from reversibility will be compounded, and it will also become the cause of generating of unusual appearances other than a manganic acid lithium. In order to use the manganic acid ghost whose mean particle diameter is 0.05-5.0 micrometers, and gamma-Mn 2O3 preferably compounded at the wet reaction as a manganese raw material in this invention, the uniform mixed state is easy to be acquired.

[0030] Primary burning temperature is 850-1000 degrees C. In the case of less than 850 degrees C, the manganic acid lithium particle powder which has high crystallinity cannot be obtained. Above 1000 degrees C, the mean particle diameter of a primary particle becomes large too much, and it is hard coming to generate the ejection and insertion of Li ion. 880-1000 degrees C is 900-1000 degrees C more preferably.

[0031] In this invention, the temperature is lowered to the temperature of secondary baking as it is after primary baking.

[0032] Secondary burning temperature is 700-800 degrees C. It is not desirable in order for detailed LiMn 2O4 to generate in the case of less than 700 degrees C and to fall the cycle property in an elevated temperature especially. When exceeding 800 degrees C, since the content of Li2MnO3 increases, it is not desirable. It is 720-780 degrees C preferably.

[0033] The firing environments of said primary baking and secondary baking is good in oxygen content gas, for example, air. Although what is necessary is just to choose firing time so that a reaction may advance to homogeneity, 1 - 20 hours is desirable.

[0034] When it calcinates in a 850-1000-degree C temperature requirement, there are many amounts of survival of Li2MnO3, and initial capacity decreases. Moreover, when it calcinates in a 700-800-degree C temperature requirement, the manganic acid lithium particle powder of a high crystal cannot be obtained.

[0035] After performing secondary baking, it grinds and manganic acid lithium particle powder is obtained.

[0036] When manufacturing positive-electrode material, using the manganic acid lithium particle powder concerning this invention as positive active material for nonaqueous electrolyte rechargeable batteries, it can mix with binding material, such as electric conduction agents, such as acetylene black and carbon black, and polytetrafluoroethylene, and polyvinylidene fluoride, etc., and can fabricate and use for a predetermined configuration.

[0037] Moreover, although especially a negative-electrode active material is not restricted, for example, the matter which can occlusion emit a lithium metal, a lithium alloy, and a lithium can be used, for example, a lithium/aluminium alloy, a lithium / tin alloy, graphite, a graphite, etc. are mentioned.

[0038] Moreover, although especially an electrolyte is not restricted, either, what dissolved at least one sort of lithium salt, such as 4 lithium perchlorate and lithium borate fluoride and a 6 phosphorus-fluoride acid lithium, can be used, for example into at least one kind of ether, such as carbonate, such as propylene carbonate, diethyl carbonate, and dimethyl carbonate, and dimethoxyethane, of organic solvent.

[0039]

[Embodiment of the Invention] The gestalt of typical operation of this invention is as follows.
[0040] The X diffraction (alpha 40kV [of RIGAKU Cu-K] 40mA) investigated identification, the crystal structure, and microcrystal size of resultant powder.
[0041] Moreover, about the gestalt of the particle of a precursor, it observed with the transmission electron microscope (Hitachi make).
[0042] The BET specific surface area was measured with the BET adsorption method.
[0043] <Production of positive electrode> manganic acid lithium particle powder, the acetylene black which is an electric conduction agent, and the polyvinylidene fluoride which is binding material were mixed at a rate of the weight ratio 85:10:5, the N-methyl-2-pyrrolidone was added and pasted, this paste was applied to aluminium foil by 0.15mm thickness, after desiccation, it pierced in the disk with a diameter of 16mm, and the positive electrode was produced.
[0044] To the negative electrode, it pierced at the 16mm disk using the lithium foil.
[0045] The <production of rechargeable battery> separator consisted of a product made from polyethylene, and pierced this to 19mm discoid. What mixed the ethylene carbonate (EC) which makes LiPF6 a supporting electrolyte, and diethyl carbonate (DEC) by the volume ratio 1:1 was used for the electrolytic solution. And the coin mold cel cell was produced all over the glove compartment of an argon ambient atmosphere.
[0046] The charge-and-discharge cycle trial of a rechargeable battery made current density to a positive electrode 0.5 mA/cm2 using said cell cel, and cut-off voltage repeated charge and discharge between 4.5V and 3.0V. It measured under the temperature of 20 degrees C and 60 degrees C.
[0047] As a <manufacture of manganic acid lithium particle powder> start raw material, 0.040 mols and 0.023 mols (Li/Mn=0.575) of lithium carbonates were mixed for gamma-Mn 2O3 created by wet composition of 0.1 micrometers of mean diameters using the automatic mortar. Primary baking was performed for the obtained mixed powder at 950 degrees C among the air air current for 3 hours.
[0048] Subsequently, it cooled to 750 degrees C and secondary baking was performed at 750 degrees C for 5 hours. After baking, it ground and manganic acid lithium particle powder was obtained. As for the obtained manganic acid lithium particle powder, the diameter of an average major axis was [1.3 micrometers and the BET specific surface area value of the peak intensity of the field (133) of 1.0m2/g and a Li2MnO three phase circuit] 0.026 to the intensity ratio of the field (400) of LiMn 2O4.
[0049] Next, the coin mold cel cell was produced using the obtained manganic acid lithium particle powder. In the 60-degree C above-mentioned conditions, initial discharge capacity was 120 mAh/g, and the maintenance factor of discharge capacity to initial discharge of 20 cycle eye of the cell property was 97%.
[0050]
[Function] The manganic acid lithium particle powder which the most important point requires for this invention in this invention is the point that charge-and-discharge capacity and a charge-and-discharge cycle property maintain balance by high order origin, when it has high crystallinity and it is moreover used as positive active material of a rechargeable battery.
[0051] The thing and those [this invention] who are because manganic acid lithium particle powder with big microcrystal size can finally be obtained by obtaining a crystalline high manganic acid lithium in order that having crystallinity with expensive manganic acid lithium particle powder in this invention may calcinate at high temperature by primary baking, and calcinating in the temperature requirement to which the crystallinity of the manganic acid lithium generated by primary baking also in secondary baking is not reduced think.
[0052] When the manganic acid lithium particle powder concerning this invention is used as positive active material of a rechargeable battery, both charge-and-discharge capacity and a charge-and-discharge cycle property are excellent, Since having secured charge-and-discharge capacity and having made high the crystallinity of said LiMn 2O4 by making [many / as possible] the content of LiMn 2O4 and Li2MnO3 can be made to contain in the range in which charge-and-discharge capacity is not reduced, the thing and those [this invention] who are because a reaction with the electrolytic solution is controlled as much as possible think.
[0053]
[Example] Next, an example and the example of a comparison are shown.
[0054] Manganic acid lithium particle powder was obtained like the gestalt of implementation of said invention except having changed various examples 1-3, the example 1 of a comparison - 3 primary burning temperature, and secondary burning temperature.
[0055] The example 1 of a comparison performed baking at 900 degrees C among the air air current for 10 hours using the same mixed powder as an example 1. In the example 2 of a comparison, it produced like the example 1

except having made primary burning temperature into 900 degrees C, and having made secondary burning temperature into 600 degrees C. In the example 3 of a comparison, it produced like the example 1 of a comparison except having made burning temperature into 750 degrees C.

[0056] The result of the manufacture conditions at this time, many properties of the obtained manganic acid lithium particle powder, and cell evaluation is shown in Table 1.

[0057]

[Table 1]

	焼成温度		粉体特性				電池特性(60℃)	
	一次焼成温度	二次焼成温度	粒子サイズ	強度比	結晶子サイズ	BET	初期放電容量	容量維持率
	℃	℃	μm	—	Å	m^2/g	mAh/g	%/20cycle
実施例1	950	750	1.2	0.026	1113	1	120	97
実施例2	900	750	0.7	0.016	909	1.1	122	96
実施例3	850	750	0.4	0.011	706	3.2	123	94
実施例4	1000	750	2.0	0.038	1450	0.8	118	97
実施例5	900	730	0.7	0.015	905	1.1	122	95
比較例1	900	—	0.7	0.15	—	1.5	108	85
比較例2	900	600	0.7	0	896	1.1	126	91
比較例3	750	—	0.2	0	580	8.6	126	89

強度比とは、$LiMn_2O_4$の(400)面のピーク強度に対するLi_2MnO_3の(133)面のピーク強度の比を示す。

[0058] By the cell of the examples 1-3 of a comparison, to the capacity at the time of a charge-and-discharge cycle having deteriorated greatly, degradation of capacity is pressed down and the better charge-and-discharge cycle maintenance factor is shown by the cell of examples 1-5 so that clearly from Table 1.

[0059]

[Effect of the Invention] Since the manganic acid lithium particle powder concerning this invention has high crystallinity and can control the elution of the manganese to the electrolytic solution, when this manganic acid lithium particle powder is used as positive active material, it can offer the nonaqueous electrolyte rechargeable battery which realized high balance-ization of charge-and-discharge capacity and a cycle property.

[Translation done.]